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Kinetic Studies of Petroleum Antioxidants

ESTABLISHMENT of reliable testing procedures is one of the important problems for those who are interested in the use of additives in petroleum fuel. Since it is seldom possible to test all potential additives under the conditions of final use, it is general practice to establish some screening procedures which are designed to simulate in some fashion the conditions of actual use. Since almost by definition this involves some change of time, temperature, pressure, or concentration from those encountered in actual use, it is always important to know how a change in these variables will change the effectiveness of the additive. Predictions based on the results of screening tests generally involve considerable extrapolation of data. Perhaps the crux of the problem is how shall this extrapolation be made. Unfortunately, there is no simple answer to this question since no single method of extrapolation is suitable for all additives. Under these circumstances it is very important to know something about the chemistry involved. This article is concerned with some problems encountered in the use of antioxidants in petroleum systems.

Classes of Antioxidants

It is very important to recognize that at least three processes can be involved when it is observed that a given material acts as an antioxidant. The material may be removing or deactivating metals which would otherwise serve to catalyze oxidation. Agents that perform this function generally are called metal deactivators and the principles behind their application are well understood (15, 20). The remaining materials can generally be classed either as inhibitors or peroxide decomposers. Inhibitors generally are phenols or aromatic amines, while peroxide decomposers may have a variety of structures, but generally contain sulfur.

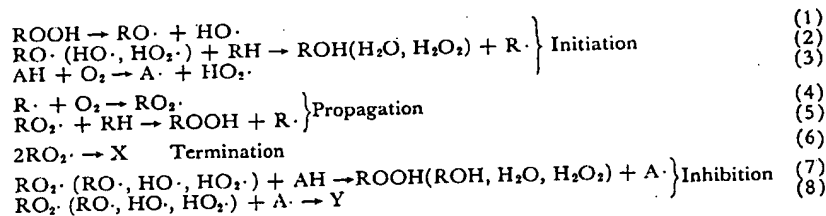
A very useful way of differentiating between these two classes is to observe the effect of adding an antioxidant to a solution containing cumene hydroperoxide by noting the rate and products of decomposition of the hydroperoxide. Three alternatives have been observed. The agent can reduce the normal rate of decomposition of cumene hydroperoxide, producing a variety of products, but no

phenol. In this case, the antioxidant is an inhibitor. Second, the agent can accelerate the decomposition and produce phenol. This is characteristic of an antioxidant which operates by peroxide decomposition. (There is also a third effect which can be observed with some materials which are not antioxidants, but rather are oxidation accelerators. The transition metals and some amines are in this class, and cause rapid peroxide decomposition but with no phenol formation.) Since these two classes of antioxidants operate by different mechanisms, it is not surprising that their end use pattern is different.

For example, antioxidants used in gasoline are generally inhibitors, while those used in lubricating oil are peroxide decomposers. It can be generalized that inhibitors will almost always prove to be superior for low temperature-low concentration applications and peroxide decomposers for high temperature-high concentration applications.

Inhibitors

The action of inhibitors can best be described by referring to the mechanism of air oxidation of hydrocarbons, first described by Criegee and coworkers (7) and Bolland and Ten Have (5).



In the absence of an inhibitor, free radicals are formed by the cleavage of any hydroperoxides present (Equation 1) or possibly by the direct attack of oxygen on the hydrocarbon. These free radicals can abstract a hydrogen atom from the hydrocarbon (Equation 2) to form an alkyl radical which reacts very rapidly with oxygen (Equation 4). The resulting peroxy radical also attacks the hydrocarbon to form a molecule of hydroperoxide and regenerate an alkyl radical (Equation 5). Steps 4 and 5 can be repeated many times with the net effect of each cycle being the consumption of a hydrocarbon molecule, and a

molecule of oxygen, and the generation of a molecule of hydroperoxide. This chain process ends with the dimerization of two peroxy radicals (Equation 6). The over-all result of this process is that one hydroperoxide molecule has been broken down to initiate free radical reactions, which in turn produce many hydroperoxide molecules. Therefore, the hydroperoxide concentration rises and the initiation rate rises with it. The whole process is thus autocatalytic and is finally limited only by the onset of secondary reactions or by depletion of the original hydrocarbon. It is generally believed that inhibitors, AH, are effective primarily because of their ability to compete with the hydrocarbon for radicals (9). Thus, Reaction 7 proceeds much more rapidly than Reaction 2 or 5. Inhibitor radicals, A·, are generally consumed directly by reaction with another radical. Thus, effectively, one molecule of inhibitor has stopped two free radical chains. The more rapid Reaction 7 is, the fewer will be the number of molecules of hydroperoxide formed before the chain is stopped. Ideally, an inhibitor would be so reactive that all free radicals would be consumed before they could react with the hydrocarbon. In this fashion the hydrocarbon would be

completely protected. If this mechanism is correct, the most effective inhibitor would be the one which could donate a hydrogen atom to a free radical most easily. Unfortunately, however, if the inhibitor hydrogen atom is very loosely bound, it can also be removed by the direct attack of oxygen on the inhibitor, as in Equation 3, to form two radicals. Therefore, it also is possible for an inhibitor to act as an initiator. Because of this, all inhibitors are a compromise between the sensitivity necessary to terminate the oxidation chains and the stability to withstand direct attack by oxygen.

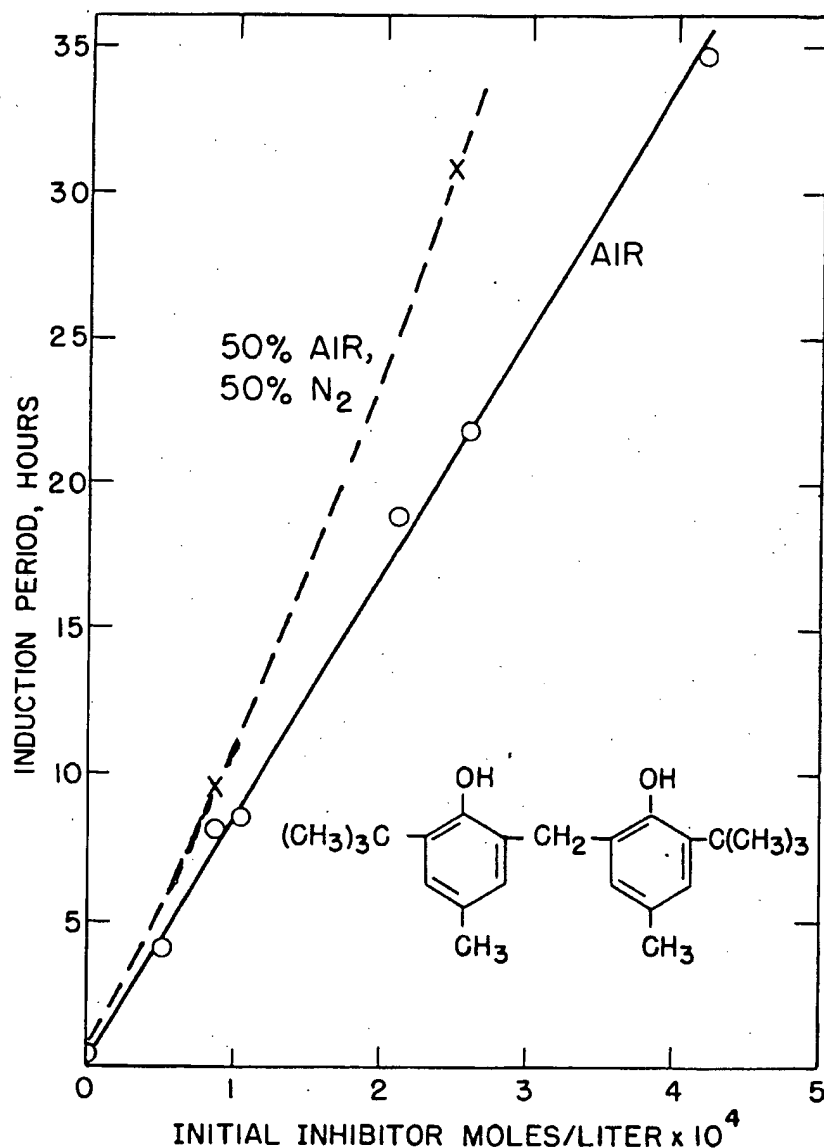


Figure 1. Inhibition of mineral oil at 155° C. by 2,2',6,6'-tetramethyl-4,4'-dihydroxybiphenyl (Initial peroxide less than 10⁻⁵ mole/liter)

Earlier workers (5) have studied the nature of inhibition in the presence of large amounts of peroxide and at very low inhibitor concentrations in easily oxidized substrates. This permitted two simplifications—all initiation results from decomposition of the added peroxide and other forms of initiation could be ignored, and, second, the rate of oxygen uptake could be measured directly, even in the presence of inhibitor. Oxygen uptake coupled with measurements of induction periods showed that, generally, many oxygen molecules reacted with hydrocarbon (Equations 4 and 5) before each chain was terminated (Equations 7 and 8). However, the problems encountered in the application of inhibitors to petroleum systems are very different. Conservation of an inhibitor dictates its addition to a system with minimum prior oxidation and, therefore,

a very low peroxide concentration. Under these circumstances, initiation may result from some process other than cleavage of peroxides. Also, petroleum products are, in general, relatively resistant to free radical attack so that it might be anticipated that inhibitors could compete relatively easily for hydroperoxide radicals and oxidation chains might be extremely short. The shorter the chains, the more significant becomes the contribution of radicals formed in the initiation processes (Equations 1 and 3) to the total radical concentration and the more important becomes a recognition of these initiation processes and the ability of the inhibitor to cope with them.

Experimental

These effects have been accentuated by a study of the oxidation of a saturated

aliphatic system—white mineral oil. In this system, oxidation rates are immeasurably low during the lifetime of an inhibitor and oxidation commences very rapidly after consumption of the inhibitor. Thus, induction periods before oxidation commences can be determined with considerable accuracy. In order to reduce the contribution of adventitious impurities which might act as inhibitors, it seemed desirable to operate at inhibitor concentrations of 5×10^{-5} mole per liter or higher. This required operation at fairly high temperatures to avoid unduly long induction periods. The general conclusions should be applicable at lower temperatures.

Procedure. A pure mineral oil (300 grams) containing the desired additives was placed in a long vertical glass tube in a thermostat, and metered air or pre-purified nitrogen was added through a sintered glass disk at the bottom. Peroxide analyses were performed on 1-ml. samples at intervals and phenol analysis was performed on a 5-ml. sample at the completion of the run. Oxygen absorption was measured in the runs using air by passing the off-gas through a Beckman Model G-2 recording oxygen analyzer and by comparing the oxygen content with frequent blank determinations on air. Induction periods were estimated from the oxygen absorption data.

Analysis. Peroxide analyses were made by the ferrous thiocyanate method of Bolland and coworkers (6). Phenol was extracted from the mineral oil solutions diluted with heptane by using 0.5N aqueous sodium hydroxide, was then acidified, and was analyzed by bromination to the 2,4,6-tribromophenol with iodimetric determination of excess bromine.

Inhibitors

Figure 1 illustrates the dependence of induction period on starting concentration of a bisphenol inhibitor in mineral oil at 155° C., with no added peroxide. The peroxide content of pure unoxidized mineral oil is beneath the limit of detection (less than 10⁻⁵ mole per liter). However, a very large excess of inhibitor over initial peroxide can be consumed by such a system, with the induction period varying linearly with inhibitor concentration (Figure 1) over a wide range of concentrations. Also, the reduction of the oxygen partial pressure to one half its former value caused a 20 to 50% increase in the induction period, depending on inhibitor concentration. It has been demonstrated many times that peroxide initiated oxidation, whether inhibited or uninhibited, is independent of oxygen partial pressure down to very low oxygen pressure. This has been confirmed for mineral oil in the presence of large amounts of its own

hydroperoxide. It must be assumed, then, that oxygen dependence in this case results from reactions of oxygen with the mineral oil or with the inhibitor which are overwhelmed when large amounts of peroxide are present. The reaction of oxygen with the inhibitor rather than with the substrate can be favored by the following example. If the starting inhibitor concentration is doubled, it would be expected that the induction period would be doubled also, if the inhibitor were consumed at the same rate as before. However, when the inhibitor concentration is raised, Reaction 7 proceeds more rapidly and is able to compete more completely with Reaction 5 for peroxy radicals. This reduces the amount of hydroperoxide formed in Reactions 4 and 5. By thus lowering the rate of formation of hydroperoxide, the hydroperoxide concentration at any given time is lowered. This lowers the rate of formation of radicals by slowing down Reaction 1. The radicals formed in Equation 1 ultimately consume inhibitor, so that reducing the rate of Reaction 1 reduces the rate of inhibitor consumption. Therefore, the over-all effect of raising the inhibitor concentration is to lower the rate of inhibitor consumption; thus doubling the inhibitor starting concentration more than doubles the induction period if Reaction 3 can be ignored. However, the rate of Reaction 3 is directly dependent on inhibitor concentration. As the inhibitor concentration is raised, Reaction 3, followed by Reactions 7 and 8, will eventually contribute significantly to total inhibitor consumption. The over-all effect of this process would be that doubling the inhibitor starting concentration would less than double the induction period.

These predictions are summarized graphically in Figure 2. Induction period is plotted as a function of inhibitor concentration. The left-hand portion of the curve represents the region in which the direct reaction of oxygen with inhibitor is not significant and where the curve would be expected to be concave upward. At the higher inhibitor concentrations, where the oxygen-inhibitor reaction predominates, the effectiveness of added inhibitor falls off rapidly. The exact manner in which these two portions of the curve would combine depends on the inhibitor being studied. Thus an inhibitor with a very easily removed hydrogen atom would be more sensitive to oxygen attack and the curve will roll off at a lower inhibitor concentration, as in the dotted curve. Also, since the reaction of oxygen with the inhibitor is proportional to the oxygen concentration in solution, the rolling off will occur at lower inhibitor concentrations if the oxygen pressure is raised.

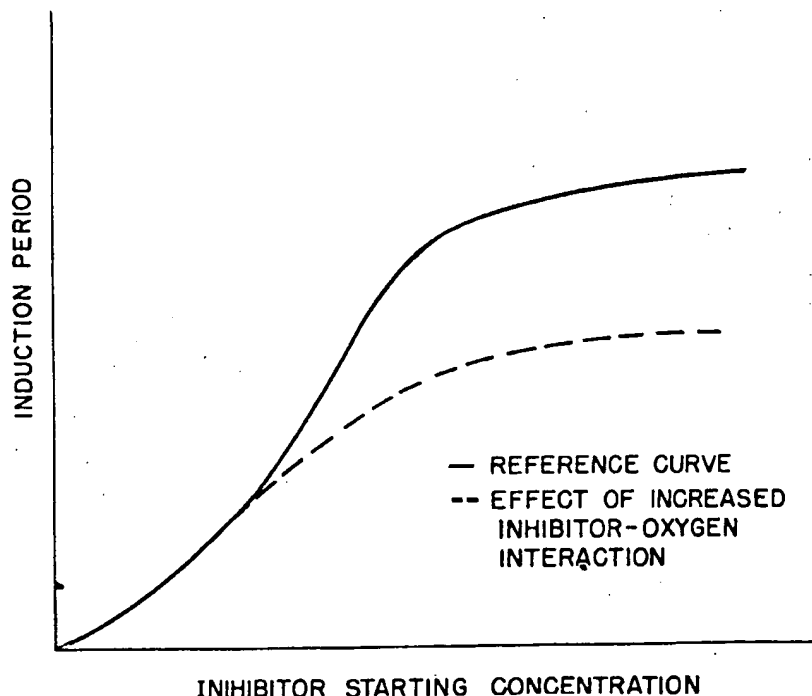


Figure 2. Predicted relationship between induction period and inhibitor concentration

Thus it appears that a linear dependence of induction period on inhibitor concentration is fortuitous, and an extension of the series shown in Figure 1 to higher concentration runs shows the rolling off predicted in Figure 2.

These results have two important applications in the testing of inhibitors. First, different inhibitors can show different concentration effects. This has been borne out by the work of Rosenwald and Hoatson (16). Also, extrapolation of results beyond the region of experimentation is dangerous unless the equations governing the dependence of induction period on concentration have been carefully evaluated. Second, the consumption of inhibitor by the direct reaction of oxygen with inhibitor may or may not be an important factor in determining the effectiveness of an inhibitor in actual practice. A screening test for antioxidants which shortens induction periods by raising the oxygen pressure can give totally misleading results. Thus the ASTM gasoline oxidation stability test, run at 100 pounds per square inch of oxygen, will multiply the rate of inhibitor-oxygen reaction by a factor of 35 over a test at the same temperature run with air at atmospheric pressure, but should not alter the rate of inhibitor-peroxide interactions. Thus the test can, in effect, measure the susceptibility of an inhibitor to attack by oxygen and not its ability to protect a system from oxidation. The probability of inhibitor-oxygen interactions was suggested many

years ago (4, 12) but its importance in the evaluation of antioxidant test results has not generally been appreciated.

Another series of induction period experiments was carried out in which inhibitor is added to mineral oil containing various amounts of mineral oil peroxides. These results are illustrated in Figure 3.

By using the data of Thomas (18) for first-order peroxide decompositions, it can easily be shown that, in all the runs of Figure 3, ample time has elapsed to permit essentially complete decomposition of the original peroxide. In the highest peroxide run, where the consumption of inhibitor by direct reaction with oxygen will be small, the total peroxide broken down amounts to 5 moles per mole of original inhibitor. It is likely that the total peroxide consumed in inhibition reactions is only 2 moles per mole of bisphenol, or two free radicals per phenol group, and that at least 3 moles of peroxide are consumed by induced decomposition of peroxide by peroxide radicals (2, 17). This is to be expected from the results of Thomas (18) and from similar studies by the authors of the kinetics of hydroperoxide decomposition in the presence of phenolic inhibitors. However, at the very low peroxide concentrations normally encountered in the application of antioxidants, peroxide consumption by induced decomposition will not be an important factor.

By observing the rate of oxygen pickup

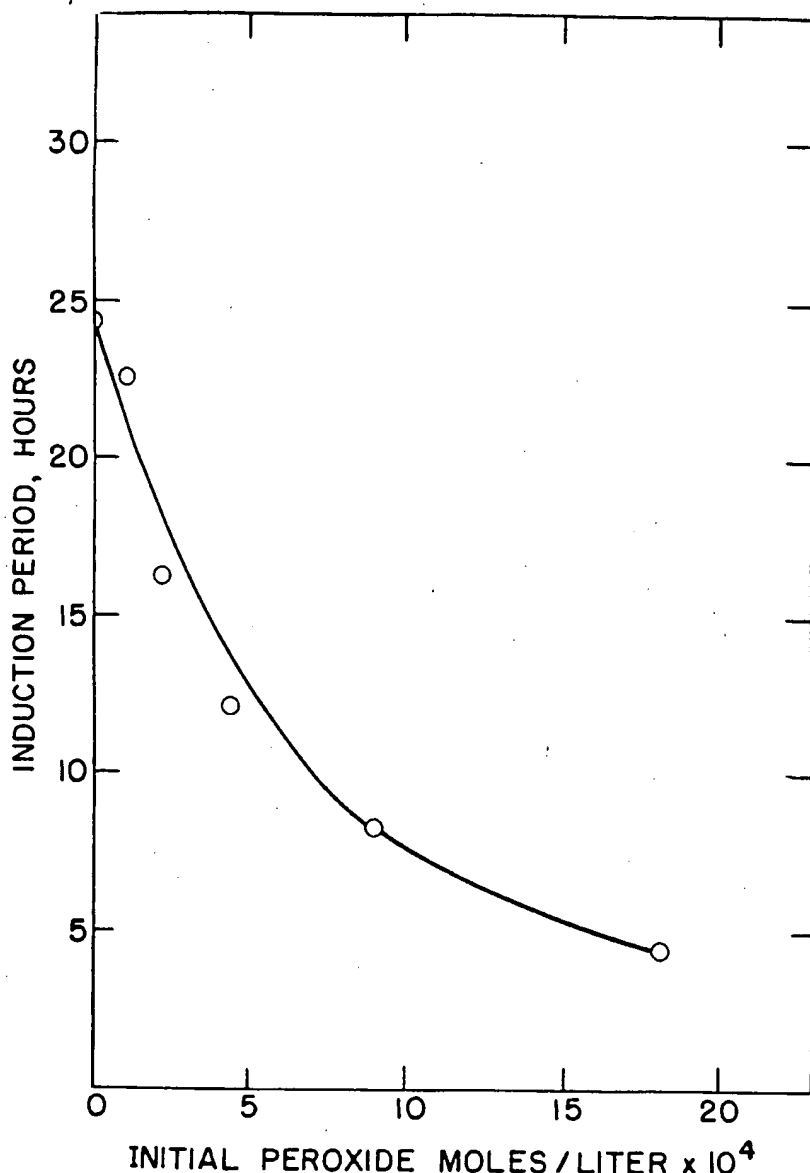


Figure 3. Effect of initial peroxide content on inhibition of mineral oil at 155° C. by 2,2'-methylenebis(4-methyl-6-tert-butylphenol)

Initial inhibitor 3.41×10^{-4} mole/liter

during a run, it is possible to detect the extent of peroxide regeneration or incompleteness of inhibition. No oxygen absorption was observed in these runs. From the limits of experimental sensitivity, it has been estimated that the molar rate of oxygen absorption must be considerably less than the rate of peroxide initiation. Thus inhibition is extremely effective, and peroxide is unable to replace itself, even in the absence of induced decomposition, until the inhibitor is largely exhausted.

While it is, in principle, possible to achieve even greater efficiency in the inhibition of free radical chains by designing inhibitors of greater sensitivity to free radical attack, it would appear that this very sensitivity makes an inhibitor more subject to direct attack by oxygen and consequent rapid consump-

tion (4, 12). A proper balance between sensitivity to free radical attack and stability against oxygen attack must be attained with due regard for the variety of conditions which an inhibitor must meet.

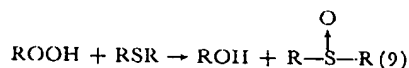
The results reported are based on high temperature oxidations purely as a matter of convenience. Since it has been shown (5) that the activation energy for the inhibiting reaction is lower than that for oxidation, a reduction in temperature should result in a closer approach to theoretical efficiency in inhibitor operation.

Peroxide Decomposers

It seems doubtful that great improvements in performance can be expected

by further improvements in free radical inhibitors. Therefore, it is desirable to consider other mechanisms whereby a system can be protected against oxidation. One such mechanism would involve catalytic decomposition of hydroperoxides initially present in a system or possibly formed as a result of the direct attack of oxygen on the substrate or on the inhibitor. It is important, however, that such a decomposition process be one in which the primary stable products are not free radicals. This rules out the decomposition of peroxides by the transition metals, particularly copper and cobalt (19).

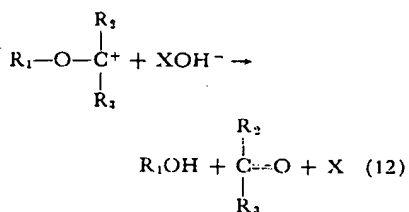
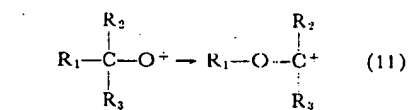
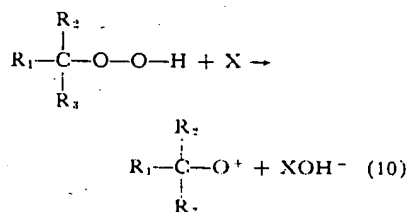
A stoichiometric process, such as that suggested by Denison (8),



would not be as desirable as an equally rapid catalytic process.

A variety of other reactions with hydroperoxides are known, which either produce free radicals or are also stoichiometric in nature (11).

The most attractive mechanism of peroxide decomposition for antioxidant application involves ionic rearrangement (10, 17) catalyzed by electrophilic reagents.



The commonest example of this reaction involves the rearrangement of cumene hydroperoxide to phenol and acetone in the presence of acid; however, a variety of other classes of compounds can catalyze this and other hydroperoxide decompositions.

Catalytic decomposition of tetralin hydroperoxide by phenothiazine has been demonstrated and has been offered as an explanation for the antioxidant activity of this compound (14), although the mechanism proposed did not suggest a rearrangement process. However, when phenothiazine is added to cumene hy-

droperoxide of phenolic peroxide. A type of air first-order rate. These effect oxide inate peroxide.

ROO

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Table Hydr at 1

n-C₁₀H₈ n-C₁₀H₈ n-C₁₀H₈

n-C₁₀H₈

RSO₂

(C₆H₅)

(C₆H₅)

HO-

CH₃C

HO-

CH₃C

HO-

CH₃C

HO-

CH₃C

HO-

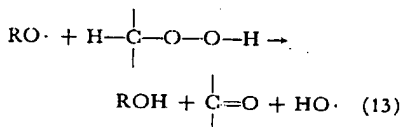
CH₃C

HO-

CH₃C

droperoxide in mineral oil, high yields of phenol are obtained, thus suggesting ionic rearrangement as the mechanism of peroxide decomposition.

A typical decomposition in the absence of air is shown in Figure 4, illustrating first-order dependence of decomposition rate on hydroperoxide concentration. These results contrast strongly with the effect of a free radical inhibitor on peroxide decomposition. Inhibitors eliminate induced decomposition of hydroperoxides (2, 17, 18), such as



and thus cause a reduction in the rate of peroxide decomposition rather than an acceleration.

A variety of sulfur-containing compounds have been tested as peroxide decomposers for preoxidized mineral oil or cumene hydroperoxide in mineral oil. First-order dependence on peroxide and inhibitor concentration has been observed, and decompositions carried out in the presence of cumene hydroperoxide have given 50 to 75% of theoretical phenol analyses. Presumably, conversion to phenol is essentially quantitative, but subsequent oxidation by unreacted hydroperoxide causes a loss in yield. Approximate rate constants, calculated

Table I. Decomposition of Cumene Hydroperoxide in White Mineral Oil at 150° C. by Sulfur Compounds

Compound	$k, \left[\frac{(\text{Liter})}{(\text{Mole})(\text{Min.})} \right]$
$n\text{-C}_{10}\text{H}_{21}\text{SH}$	500
$n\text{-C}_4\text{H}_9\text{S}-n\text{-C}_4\text{H}_9$	60
$n\text{-C}_4\text{H}_9\text{S}-n\text{-C}_4\text{H}_9$	40
$\begin{array}{c} \text{O} \\ \\ n\text{-C}_4\text{H}_9\text{S}-n\text{-C}_4\text{H}_9 \\ \\ \text{O} \end{array}$	2
RSO_3H (av. mol. wt. 500)	200
$\begin{array}{c} (\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{S})_2 \\ \\ \text{C}_6\text{H}_5\text{O} \end{array} \text{Zn}$	2000
$\text{C}_6\text{H}_5\text{S}-\text{C}_6\text{H}_5$	0.6
$\text{C}_6\text{H}_5\text{S}-\text{C}_6\text{H}_4\text{OH}$	6.0
$\text{HO}-\text{C}_6\text{H}_4\text{S}-\text{C}_6\text{H}_4\text{OH}$	60
$\text{CH}_3\text{O}-\text{C}_6\text{H}_4\text{S}-\text{C}_6\text{H}_4\text{OCH}_3$	0.00
$\text{C}_6\text{H}_5\text{SH}$	60

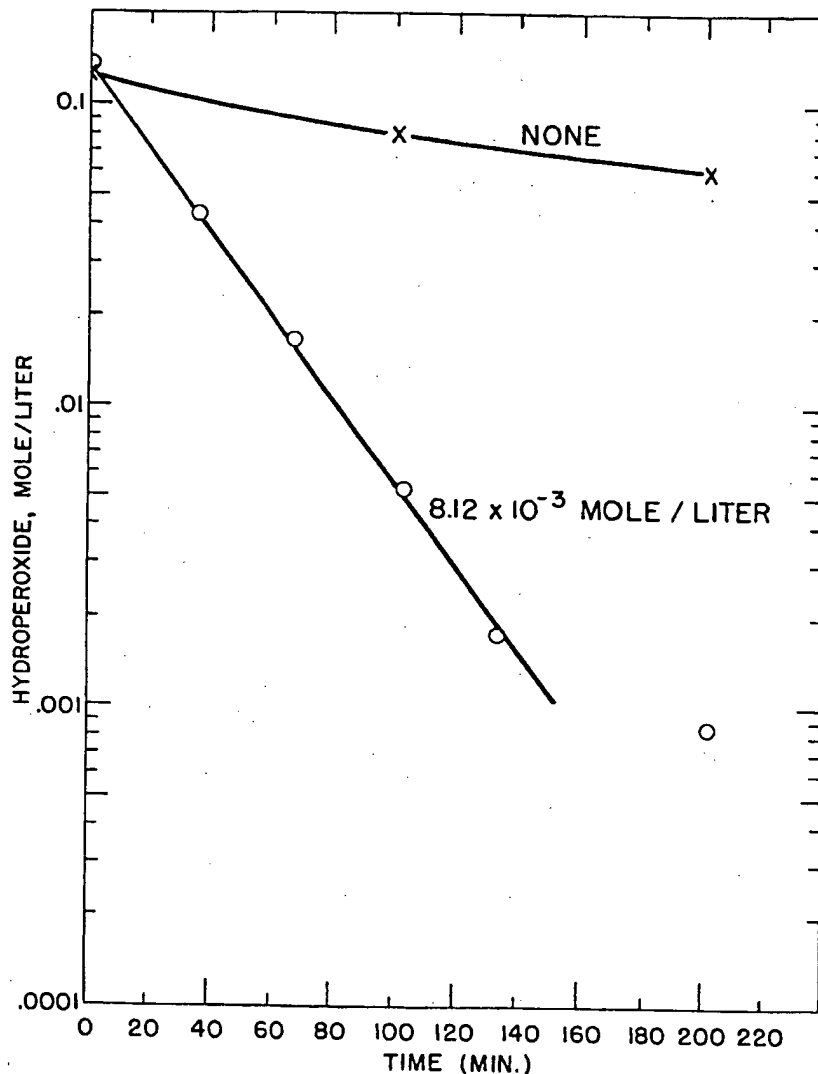
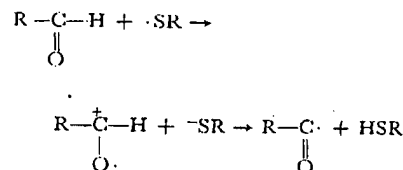


Figure 4. Decomposition of mineral oil hydroperoxides by zinc di(4-methyl-2-pentyl) dithiophosphate at 130° C.

from the decomposition rate expression $-\frac{d(P)}{dt} = k(D)(P)$, for hydroperoxide decomposition by some typical simple sulfur compounds are given in Table I. Although the activity of a sulfonic acid is to be expected from earlier work showing catalysis of cumene hydroperoxide decomposition by acids (10, 17), it is unlikely that the activity of the other compounds is due to their conversion to strong acids. No obvious process for converting phenol sulfides to sulfonic acids is known which is compatible with the dependence of activity on structure, as shown in Table I. However, short induction periods can be observed in peroxide decompositions carried out at low temperatures, and these induction periods can be extended in some cases by the addition of free radical inhibitors. Bateman and Shipley (3) have shown

that activated sulfides are oxidized initially to hydroperoxides which break down, leading eventually to inhibition of further oxidation. Thus it appears that the original structures are only precursors of active inhibitors. The active structure derived from a mercaptan may be the mercaptanyl radical, which has been suggested as the active intermediate in the mercaptan-catalyzed decarbonylation of aldehydes (7, 13). The transfer of one electron from aldehyde to mercaptan is believed to be an intermediate in the process.



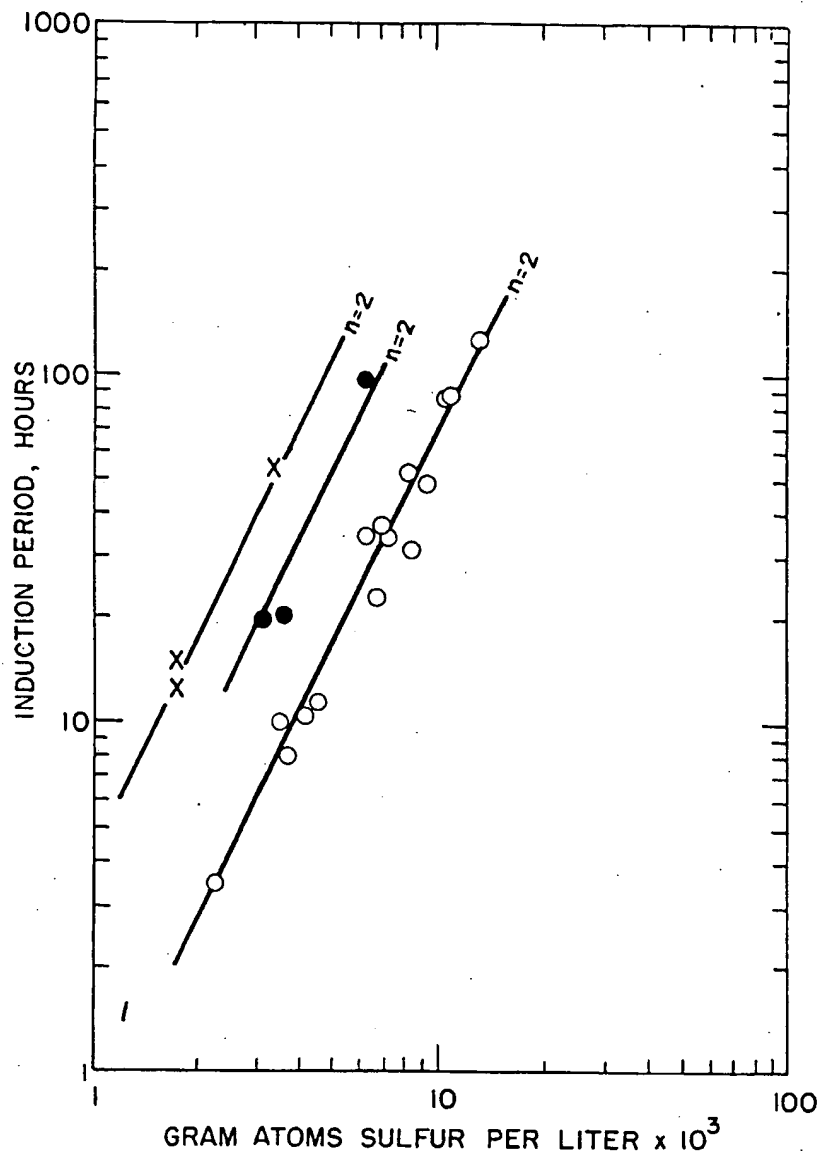
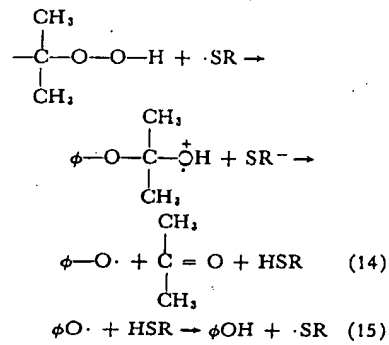


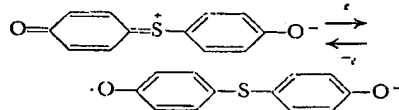
Figure 5. Induction periods for mineral oil at 155° C. as function of initial concentration of peroxide decomposer

X = Zn di(4-methyl-2-pentyl) dithiophosphate
 ● = N,N'-Dibenzoyl di-o-aminophenyl disulfide
 ○ = Sulfurized butyl ester of tall oil fatty acids

by a similar process, an electron-deficient hydroperoxide might be expected to rearrange:



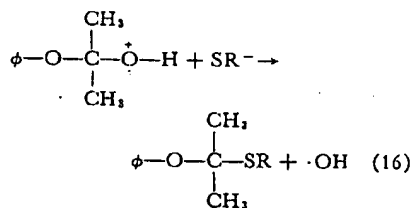
Electron transfer reactions in the phenol disulfide series may occur between the following structures:



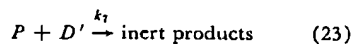
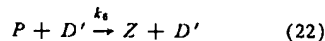
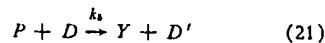
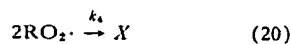
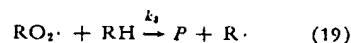
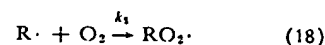
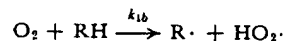
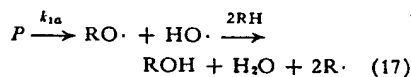
Furthermore, when a hydroperoxide decomposition is carried out in the presence of air, a moderate increase in the rate of oxidation is observed until the hydroperoxide concentration has been reduced by the decomposition process. This suggests the occasional incursion of free radical processes in the decomposition and supports the concept of one electron transfer reactions.

Kharasch and coworkers (17) have observed that acid-catalyzed decomposition of cumene hydroperoxide is a chain reaction and that the addition of anions reduces the rate of the process, presumably

by shortening the chains. The same phenomenon is observed in our work. The consumption of peroxide decomposer in the same fashion could occur by Reaction 16 which terminates the chain. It is of particular interest to consider how a peroxide decomposer



might provide protection to a system containing no added peroxide. As a first approximation, it can be assumed that a peroxide decomposer does not enter significantly into the normal oxidation chains, but reduces oxidation by holding the peroxide concentration at a very low level, thus reducing the rate of the initiation. It can be assumed further that the mechanism of Equations 14 to 16 holds generally.



where P = hydroperoxide, D = original structure of peroxide decomposer, and D' = active form of peroxide decomposer.

From this series of rate steps, the following kinetics can be derived when $k_{1a}(P) \gg k_{1b}(\text{O}_2)(\text{RH})$

$$-\frac{d\text{O}_2}{dt} = k_m P^{1/2} \quad \text{where } k_m = \frac{k_2 k_1^{1/2}}{k_4^{1/2}} [\text{RH}] \quad (24)$$

$$\frac{d(D')}{dt} = k_5(P)(D) - k_7(P)(D') = 0 \quad (25)$$

$$(D') = \frac{k_5}{k_7}(D)$$

$$\frac{dP}{dt} = k_m(P)^{1/2} - k_6(P)(D') = 0 \quad (26)$$

$$(P)^{1/2} = \frac{k_m}{k_6(D')} = \frac{k_m k_7}{k_6 k_5(D)}$$

$$P = \frac{k_m^2 k_7^2}{k_6^2 k_5^2 D^2}$$

$$-\frac{d(D)}{dt} = k_6(P)(D) = \frac{k_m^2 k_7^2}{k_6 k_5^2 D} \quad (27)$$

Equation establish if it is a and the Equation rate of oxygen peroxide nating 1 in Equa are set e state a velops b This giv the indu to the se of decor ation is state per and init gen on s derivati period s power c compost intuitive period i of the de version peroxid decomp peroxid do not c be used

The oxidant oxidatic of sulfur are kno compose = $n \log$ vs. \log example slope of disulfide slope o and n -d disconti concent gram at oxygen for the develop dant co breakdc build-up the an process sumptio formanc state as

$$D = \sqrt{D_0^2 - \frac{2k_m^2 k_7^2 t}{k_3 k_6^2}}$$

$$D = D_0 \text{ when } t = 0$$

$$D = 0 \text{ when } t = t_{\text{ind.}} \quad (28)$$

$$t_{\text{ind.}} = \frac{k_3 k_6^2}{2k_m^2 k_7^2} D_0^2 = k' D_0^2$$

Equation 24 is the standard equation established for uninhibited oxidation, if it is assumed that the chains are long and the peroxide concentration is low. Equation 26 follows, since $k_m P^{1/2}$ is the rate of oxygen absorption and each oxygen molecule absorbed forms a peroxide. Chain initiating and terminating reactions are assumed negligible in Equation 26. Equations 25 and 26 are set equal to zero by the usual steady-state assumption. Equation 27 develops by simple algebra and integration. This gives the very interesting result that the induction period will be proportional to the square of the initial concentration of decomposer as long as peroxide initiation is predominant. If the steady-state peroxide concentration is very low and initiation by the direct attack of oxygen on substrate predominates, a similar derivation shows that the induction period should be proportional to the first power of the initial concentration of decomposer. Equation 28 also illustrates an intuitively obvious point. The induction period is determined by three properties of the decomposer—its initial rate of conversion to the active form, k_3 , rate of peroxide decomposition, k_6 , and rate of decomposer consumption, k_7 . Since peroxide decomposition measurements do not evaluate third factor, they cannot be used to predict induction periods.

The effect of concentration of antioxidant on the induction period for oxidation has been studied for a variety of sulfur-containing compounds which are known to be effective peroxide decomposers. If $t_{\text{ind.}} = kP^n$, then $\log t_{\text{ind.}} = n \log P + \log k$, and a plot of $\log t_{\text{ind.}}$ vs. $\log P$ has a slope n . Several examples, plotted in Figure 5, show a slope of 2, while in Figure 6 di-*n*-decyl disulfide at high concentrations has a slope of 1. Both di-*n*-decyl disulfide and *n*-decyl mercaptan show a virtual discontinuity for induction period as the concentration is raised above 6×10^{-3} gram atom of sulfur per liter. A plot of oxygen absorption versus time shows that, for these two antioxidants, activity develops slowly, so that at low antioxidant concentrations, oxidation prior to breakdown causes an initial peroxide build-up which must be decomposed by the antioxidant. This decomposition process leads to high antioxidant consumption, and consequent poor performance. For such examples, steady-state assumption of Equation 31 is not

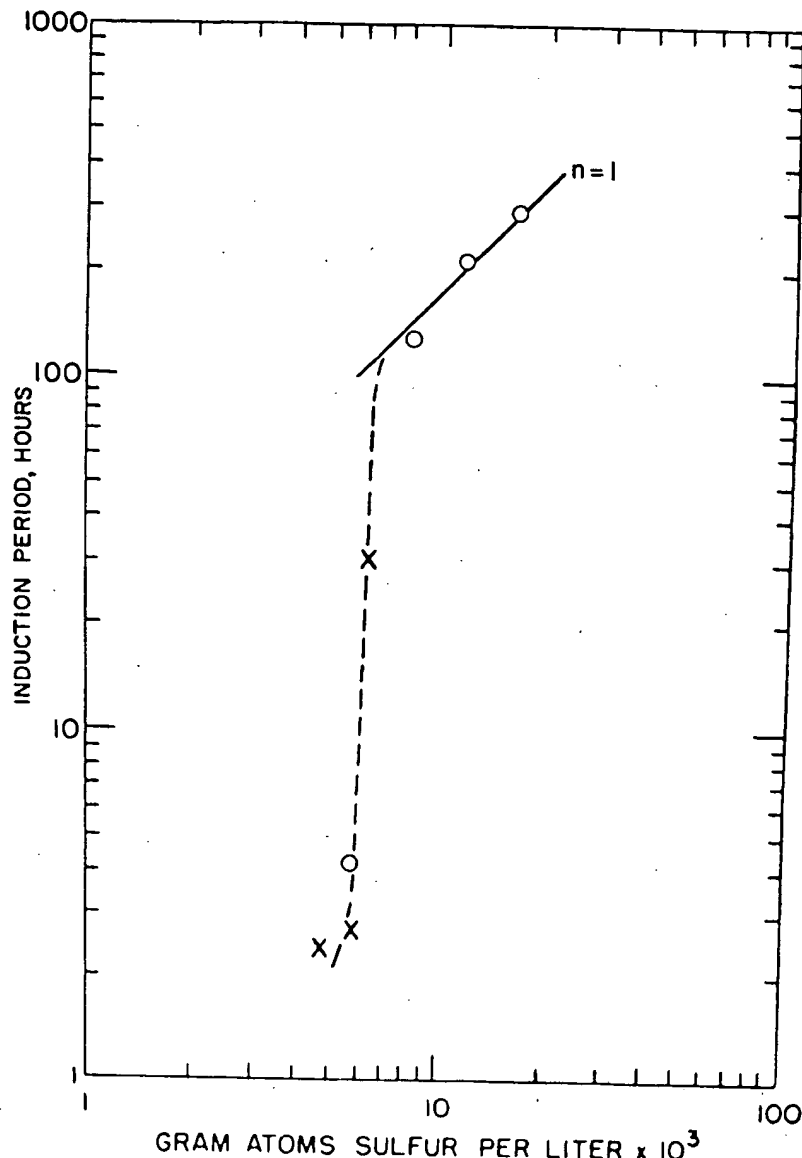


Figure 6. Induction periods for mineral oil at 155° C. as function of initial concentration of peroxide decomposer

○ = Di-*n*-decyl disulfide
X = *n*-Decyl mercaptan

valid and the kinetics cannot be solved.

It is again evident that induction periods may vary with concentration in a different manner for two different antioxidants, thus illustrating the danger of comparing the performance of two antioxidants under conditions and concentrations not those of intended application.

Qualitatively, however, some generalizations are possible. Free radical inhibitors, in the comparative absence of initial peroxides, generally confer stability for periods of time approximately in direct proportion to their concentration, while peroxide decomposers tend to show greater concentration dependence. Thus at high treating concentrations, peroxide decomposers become relatively

more effective than free radical inhibitors, and, at low concentrations, relatively less effective.

In general terms, these conclusions are supported by practical experience in the stabilization of petroleum products against oxidation. When conditions are severe and high concentration of an antioxidant is required, peroxide decomposers provide superior protection. This is particularly true in automotive lubricating oils, where high temperatures are encountered, and starting peroxide concentration may be appreciable if the drained oil is badly oxidized and not completely flushed before refilling. All of the commonly used lubricating oil antioxidants are, in fact, peroxide

Table II. Stabilization of Mineral Oil at 155° C.

Inhibitor	Peroxide Decomposer	Decomposer Concn., %	Induction Period, Hours, at Inhibitor Concn., %		
			0.0	0.0033	0.0067
2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	Zn di(4-methylpentyl-2) dithiophosphate	0.0	0.5	6.0	12.7
		0.0063	..	32.0	...
		0.025	12.7	...	55.0
2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	Di- <i>n</i> -decyl sulfide	0.00	0.5	...	12.7
		0.025	12.2	...	54.7
<i>N,N'</i> -Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	Zn di(4-methylpentyl-2) dithiophosphate	0.00	0.5	...	16.1
		0.025	12.7	...	38.2

Table III. Stabilization of Mineral Oil at 180° C.

Inhibitor	Peroxide Decomposer	Decomposer Concn., %	Induction Period, Hours, at Inhibitor Concn., %		
			0.00	0.10	0.20
2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	Zn di(4-methylpentyl-2) dithiophosphate	0.00	0	...	14.5
		0.10	..	13.5	31.0
		0.20	1.5	15.5	...

Table IV. Stabilization of Mineral Oil at 155° C.

Inhibitor A	Inhibitor B	Induction Period, Hours at Inhibitor A Concn., %	
		0.0	0.0067
2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butyl-phenol)	<i>N,N'</i> -Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	0.0	0.5
		0.0067	16.1
			17.0

Table V. Stabilization of Mineral Oil at 155° C.

	Induction Period, Hours, at Di- <i>n</i> -decyl Disulfide Concn., %	0.000	0.084
2,2'-Methylene-bis(4-methyl-6- <i>tert</i> -butylphenol), %	0.0	0.5	0.5 (65.0°)
Zn di(4-methylpentyl-2) dithiophosphate, %	0.025	12.7	48.3
	0.0067	12.7	112.0

^a Extrapolated.

decomposers. On the other hand, the stabilization of gasoline in storage can be accomplished by the use of very small amounts of antioxidant, added to gasoline before appreciable build-up of peroxides can occur. In these circumstances, free radical inhibitors are advantageous and, in practice, all commonly used gasoline antioxidants are free radical inhibitors. There are, however, a variety of applications in which conditions are moderately severe. For these applications a choice between two classes cannot be made arbitrarily.

Synergistic Effects with Inhibitor-Peroxide Decomposer

A further consideration of the proposed differences in mechanism for free radical inhibitors and peroxide decomposers leads to another interesting conclusion. If peroxide decomposers do not inhibit

free radical chain reactions but depress oxidation only by destroying most of the peroxide before it can initiate chains, it might be expected that the further addition of a free radical chain inhibitor could prevent even this oxidation and thus conserve the effectiveness of the peroxide decomposer. Conversely, the peroxide decomposer, by decomposing those peroxides which are formed in spite of the presence of an inhibitor, reduces the amount of chain initiation and, consequently, the amount of inhibitor consumption.

Thus, synergistic effects can be expected when an inhibitor and a peroxide decomposer are used in combination under conditions in which each is somewhat effective. Such synergism has been confirmed for a wide variety of combinations of inhibitor-peroxide decomposer. Examples are given in Tables II to IV.

In contrast to this behavior, the

combination of two inhibitors shows, at best, additive rather than synergistic effects, and can show antagonistic effects, as in Table II. Results with combinations of two peroxide decomposers can be difficult to interpret, since unusual concentration dependence is sometimes observed with these agents. Some synergism for combinations of peroxide decomposers has been observed, but to a lesser degree than can be achieved by replacing either by an inhibitor (Table V).

The suggestion that peroxide decomposers would prove to be ineffective relative to free radical inhibitors in low concentration is borne out in tests carried out at 100° C. or below using easily oxidized systems such as thermally cracked gasoline. High concentrations of peroxide decomposers in more stable hydrocarbons may well show the same properties at low temperatures as observed at higher temperatures, but induction periods are too long for convenient experimentation and have not been studied.

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